

PTO 08-0531

CC=EP
DATE= 20010502
KIND= Patent
PN= 1095993

PROCESS FOR CONTINUOUS PRODUCTION OF SELF-ADHESIVE ARTICLES
BY COATING OF WEB-SHAPED INCOMING MATERIALS WITH TWO-
COMPONENT POLYURETHANES

[VERFAHREN ZUR KONTINUIERLICHEN HERSTELLUNG VON
SELBSTKLEBENDEN ARTIKELN DURCH BESCHICHTUNG VON
ZULAUFENDEN BAHNFÖRMIGEN MATERIALIEN MIT
ZWEIKOMPONENTIGEN POLYURETHANEN

SCHÜMMANN UWE, WAPPLER ULRIKE, HIRSCH RALF, BECKMANN ANDREAS,
BERNOTH ANDREE

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. OCTOBER 2007
TRANSLATED BY SCHREIBER TRANSLATION, INC.

| | | |
|-------------------------------|--------|--|
| PUBLICATION COUNTRY | (10): | EP |
| DOCUMENT NUMBER | (11): | 1095993 |
| DOCUMENT KIND | (12): | Patent |
| PUBLICATION DATE | (43): | 20010502 |
| APPLICATION NUMBER | (21): | 001219971 |
| APPLICATION DATE | (22): | 20001010 |
| INTERNATIONAL CLASSIFICATION | (51): | C09J 7/02 |
| PRIORITY COUNTRY | (33): | |
| PRIORITY NUMBER | (31): | |
| PRIORITY DATE | (32): | |
| INVENTOR(S) | (72): | Schümann, Uwe, Dr. 25421 Pinneberg (Germany); Wappler, Ulrike, 20253 Hamburg (Germany); Hirsch, Ralf, 25451 Quickborn (Germany); Beckmann, Andreas 22609 Hamburg (Germany); Bernoth Andree 22299 Hamburg (Germany) |
| APPLICANT(S) | (71): | Beiersdorf Aktiengesellschaft, 20245 Hamburg (Germany) |
| DESIGNATED CONTRACTING STATES | (81): | |
| TITLE | (54): | PROCESS FOR CONTINUOUS PRODUCTION OF SELF- ADHESIVE ARTICLES BY COATING OF INCOMING WEB-SHAPED MATERIALS WITH TWO-COMPONENT POLYURETHANES |
| FOREIGN TITLE | [54A]: | VERFAHREN ZUR KONTINUIERLICHEN HERSTELLUNG VON SELBSTKLEBENDEN ARTIKELN DURCH BESCHICHTUNG VON ZULAUFENDEN BAHNFÖRMIGEN MATERIALIEN MIT ZWEIKOMPONENTIGEN POLYURETHANEN |

Description

[0001] This invention relates to a process for continuous production of self-adhesive articles like for example, self-adhesive tapes by coating of an incoming, web-shaped material or of two simultaneously incoming, web-shaped materials which are arranged parallel to one another but are not in contact with each other, with a reactive, two-component polyurethane-substrate, whereby at least one of the incoming, web-shaped materials is provided with a pressure-sensitive adhesive mass (self-adhesive mass).

[0002] Single-sided, self-adhesive articles comprise at least two layers (plies), namely the substrate layer which is not self-adhesive and the pressure-sensitive adhesive mass which is applied to it. A double-sided adhesive tape is generally made up of at least three layers, namely the substrate and the adhesive layers that are applied to the substrate on both sides. Exceptions are double-sided, self-adhesive articles for which the substrate and the adhesive layer are identical (so-called, single-layer products).

[0003] The mechanical properties of an adhesive tape (for example, tensile strength, extensibility, elasticity) are predominantly determined by the substrate. Moreover, the substrate largely determines the optical properties of an adhesive tape (transparency, color) and the surface properties of the not self-adhesive side in case of a single-sided, self-adhesive article (structure, roughness, surface tension). The substrate also determines the adhesive properties of a self-adhesive article.

[0004] All web-shaped materials can be considered as substrates, for example, paper, fabric, mats, films or elastomers, in varying thickness, structures and polymer compositions.

[0005] The adhesive layer considerably determines the adhesive properties of a self-adhesive article in combination with the used substrate, which are manifested in shear endurance, bond strengths, tilting-shear behavior, winding-up behavior, detachability, etc amongst others.

[0006] Base-polymers of modern adhesives are, amongst others, natural and synthetic rubbers, polyacrylates, block copolymers with polystyrene block parts, polyethylene vinyl acetate and polyurethane which are used mostly in combination with additives like resins and plasticizers and/or other materials like for example, anti-oxidants, UV-protective agents or rheological additives.

[0007] The usually used process for manufacture of adhesive tapes comprises coating of a separately manufactured, web-shaped substrate material with an adhesive mass. The coating takes place mostly with a solution, i.e. the adhesive mass is converted into a spreadable consistency before coating by using solvents.

[0008] The coating can be undertaken even – depending on the polymer composition – from the melt without using solvent in an extrusion process. This process has been established especially in case of adhesives based on thermoplastic elastomers.

[0009] Further, the bonding of substrate and adhesive mass can be undertaken even by first applying the adhesive mass on a dehesive medium and subsequently applying on the substrate in a coating process.

[0010] The coating of web-shaped substrate materials with adhesive masses as a process for production of self-adhesive articles is very well established.

[0011] Nevertheless, there are a number of fundamental disruptive disadvantages that are noticeable especially in case of adhesive tapes with high or very special requirement profiles. Thus, in many cases, the anchoring of adhesive mass on the substrate is problematic and requires another process step, namely, the coating with a primer (pre-coat). In case of a double-sided adhesive tape, this is obviously done on both sides resulting in a product structure of five layers. Further, no custom-designed substrate is available in the market required for special applications. Then, either the bonding system is used which is made up of individual substrates which must be joined for e.g. with primer- and adhesive systems or by applying additional auxiliary layers (for e.g. barrier layers to prevent migration of ingredients from the substrate into the adhesive layer or mirror layers for smoothening of rough substrate surfaces). All this results in increased complexity in the manufacturing process and thus, increased production costs.

[0012] Some adhesive tapes are depicted in the text below from the comprehensive prior art, especially those in which polyurethane or polyurethane films are used as substrate material.

[0013] WO 86/00536 A1 describes a laminate obtained from a polyurethane and a pressure-sensitive adhesive layer, whereby the laminate is used for pellet packing, and also in the administration form. A polyurethane film, without further treatment, is provided with a self-adhesive coating which encloses a pellet and simultaneously bonds to the pellet to the skin of the user.

[0014] In US 5,127,974 A, a laminate made from polyurethane film with a self-adhesive coating is mentioned. This laminate is especially used for temporary protection of coated surfaces of automobiles.

/3

[0015] A pressure-sensitive adhesive tape coated on both sides with adhesive mass is known from DE 196 14 620 A1 and DE 197 33 014 A1; its substrate is made from a formulated, cross-linked, unfoamed polyurethane.

Formulation constituents of the substrate are: a cross-linked, unfoamed polyurethane, fillers and if necessary, other auxiliary substances.

According to DE 196 14 620 A1, the portion of polyurethane on the substrate is up to 50% by weight, preferably 30% by weight to 40% by weight, whereby the polyurethane is free from plasticizers. The fillers make up 50% by weight to 70% by weight of the substrate.

According to DE 197 33 014 A1, the portion of polyurethane on the substrate is up to 50% by weight, preferably 10% by weight to 40% by weight. The fillers make up 40% to 70% by weight of substrate, while the plasticizers and resins together are 5% by weight to 30% by weight, especially 10% by weight to 25% by weight.

The choice of isocyanate- components of polyurethane depends on the specific properties of the substrate to be adjusted. These can be for e.g. toluylene diisocyanate, diphenylmethane-4, 4'- diisocyanate, dicyclohexyl methane-4, 4'- diisocyanate, hexamethylene diisocyanate, isophoron diisocyanate, mixtures of the mentioned isocyanates or chemically derived isocyanates, for e.g. dimerized or trimerized types.

The choice of components reacting with the isocyanate depends on the properties of the substrate that are to be adjusted depending on the desired requirement profile.

For example, all polyester dioles, -trioles and -polyoles, polyether dioles, -trioles and -polyoles, polyether diamines, -triamines, -polyamines, hydroxyl-functionalized polybutadienes and all monovalent alcohols (mono-oles), monovalent amines (mono-amine), polyether-mono-ole, polyether-mono-amine or products that have been derived from the last four mentioned groups are used.

It has proven to be advantageous if hydroxyl-functionalized polybutadienes, polyester dioles, polyester trioles, polyester polyoles, polyether dioles, polyether trioles, polyether polyoles, polyether diamines, polyether triamines or polyether polyamines have a molecular weight $M_g \geq 1000$ g/mol.

[0016] The task of this invention is to develop a process with which self-adhesive articles can be produced continuously without having to manufacture the web-shaped substrate of self-adhesive article separately and finally, the self-adhesive article must be coated with an adhesive mass with direct application or by a coating process such that the fundamental disadvantages of the traditional manufacturing process for adhesive tapes cannot occur in this form. The substrate must have an excellent property profile that can be varied and adjusted diversely.

[0017] This problem is solved by a process as depicted in the main claim. The objectives of the sub-claims are advantageous developments of this process. Finally, the underlying thought of the invention includes even self-adhesive articles that are manufactured according to the inventive process.

[0018] Accordingly, in the text below, the invention describes the process for continuous production of self-adhesive articles whose substrate contains a polyurethane as the base polymer:

[0019] The inventive process consist of the following individual steps:

- a) a polyol- component is taken in a container A and an isocyanate- component is taken in a container B,
- b) the polyol- and isocyanate-components are mixed in a mixer,
- c) the polyurethane mass thus mixed is applied on a substrate which is coated with a pressure-sensitive adhesive mass; this substrate moves preferably at constant speed,
- d) the laminate, comprising of first substrate, adhesive mass and polyurethane mass is passed through a heated channel in which the polyurethane mass is hardened,
- e) the laminate is finally wound up in a winding station.

[0020] In a preparatory step, the substrate is provided with an adhesive mass on both sides or especially on one side. This is undertaken in a usual coating process, either from a solution or from a melt. The substrate can be a dehesive medium for example, a release paper or a release film. It can also be any other arbitrary substrate, for example, a paper,

fabric, mat, a film or an elastomer which constitutes a portion of the entire substrate of the self-adhesive article after the last procedural step.

[0021] For the case in which the substrate is a dehesive medium, the polyurethane mass is applied on the substrate which is coated with a pressure-sensitive adhesive mass such that the polyurethane mass lies on the pressure-sensitive adhesive mass. For the case in which the substrate is not a dehesive medium, the polyurethane mass is preferably applied on that side of the substrate which is not on the pressure-sensitive mass. Alternatively, even in this case, the polyurethane mass can be applied on the pressure-sensitive adhesive mass. If so, another layer of adhesive must be applied on the exterior side of the substrate.

/4

[0022] In another preferred embodiment of the process, a second substrate is fed at preferably constant speed to the polyurethane mass of laminate.

In another preferred embodiment of the process, the second substrate is provided with a pressure-sensitive adhesive mass.

In this case, an additional preparatory step is required in which the first preparatory step is repeated accordingly, whereby neither the adhesive mass nor the web-shaped material need to be identical to those of the first preparatory step.

If necessary, after the heated channel, the second substrate is peeled off.

[0023] Further, it is advantageous if many containers are made available upstream of the mixer in which catalysts, plasticizers, dyes and other additives may be introduced and added.

[0024] The coating with the reactive, two-component polyurethane on the first substrate is undertaken preferably in a standard coating plant for the production of adhesive tapes. Such a plant in a preferred embodiment is shown in Figure 1.

[0025] The plant 100 has two bale unwinders 11, 12 for the incoming materials 1 and 2, further, it also has a product winding station 21 and a bale winder 22 for an auxiliary material 3 that may be uncovered. Further, the unit 100 has a heated channel 31 in which the hardening of polyurethane mass 4 takes place.

The incoming web-shaped materials 1 and 2 are guided in such a way that the coating of polyurethane mass 4 can be undertaken directly in the gap between both the materials 1 and 2. The width of the gap is variable and can be adjusted freely.

[0026] A web-guide, not shown here, of the second substrate 2 is placed behind the gap via a belt; this is advantageous for achieving good thickness constancy of polyurethane-substrate 4.

[0027] In case of a single-sided, self-adhesive article, the upper bale unwinder and the bale unwinder 3 for the auxiliary material to be uncovered, may be omitted.

Alternatively, a dehesive material can be used whose function is to merely keep the shaft and the reactive polyurethane from coming into contact with one another in order to avoid polyurethane- dispersion hardenings on the shaft.

[0028] The reactive polyurethane- substrate mass 4 is produced continuously directly before coating, using two components that react chemically with each other, namely a usually pre-formulated polyol- component (A) and a isocyanate –component (B) which are taken each in a container 41 and 42, in a mixing head (dynamic mixer) or in a mixing

tube (static mixer) of a customary two-component- mixing- and dosing unit 43 and this polyurethane- substrate mass is applied directly between the incoming, web-shaped materials 1 and 2.

Any commercial unit can be used as a two-component- mixing and dosing unit 43 which is suitable for casting and is designed for short pot lives of generally less than a minute. This can be achieved in a static as well as in a dynamic mixing system. In order to be able to coat the incoming materials 1 and if necessary, 2 in full width with the polyurethane- substrate material 4, it is advantageous to install the mixing head or the mixing tube on a traversing device such that it is movable; it then permanently travels the width of the incoming materials in an oscillating manner.

[0029] The reactive polyurethane mass 4 hardens to the desired substrate material in a connected heated channel section 31 and it generally binds chemically to the incoming materials, especially adhesive layers. The adhesion to an acrylate takes place for example, through the formation of carboxylic acid amide. After the channel section 31, the finished product is wound up.

The heated channel section 31 is preferably held at temperatures between 20°C and 120°C.

[0030] In case of a double-sided adhesive tape, a three-layered product structure, consisting of adhesive mass, polyurethane- substrate, adhesive mass is obtained. No primer and no other additional layer is required. The substrate thickness can be adjusted comfortably via the gap width on the commissioned workpiece. Since the polyurethane- components (A) and (B) do not contain any solvent, even very thick substrates can be produced without blow holes with this process.

In a possible embodiment, the substrate has a thickness of 0.1 to 50 mm, preferably 0.4 to 20 mm. The adhesive mass has preferably an application weight of 10 g/m² to 100 g/m².

[0031] The materials that contain polyurethane as base polymer and can be produced in a two-component mixing process can be used as polyurethane- substrate materials. The diversity of the polyurethane – chemical industry resulting from the abundance of the polyurethane- blocks prepared by the chemical raw material industry as well as from the diverse options of compounding with fillers, resins, plasticizers, other polymers like epoxides, acrylates, natural and synthetic rubber, ethylene vinyl acetates, block copolymers with polystyrene block parts and other additives like anti-aging agents, UV-protective agents or rheological additives, makes it possible to prepare customized, self-adhesive articles according to this process.

/5

[0032] Further, even all foamed materials can be considered as polyurethane- substrates which contain polyurethane as base polymer and are manufactured in a multi-component-mixing process. The foam structure can be achieved, thereby, chemically, for example by an isocyanate/ water reaction triggered during the mixing process or with a foaming agent and physically by introducing a gas (for example, nitrogen or air). The introduction of gas can be achieved directly on the mixing head of a multi-component- mixing – and dosing unit as well as during the manufacture of A- or B-component. The gas introduced in the mixing head represents, so to speak, the special case of a third component.

[0033] Reference may be made to the depiction of the state-of-the-art polyurethane - chemistry in "Plastic- manual, 7, Polyurethanes, Becker/Braun (1993)".

[0034] A possible embodiment of the substrate comprises a cross-linked, non-foamed polyurethane, fillers and if necessary, other excipients as formulation components.

The portion of polyurethane on the substrate is up to 50% by weight, preferably 30% by weight to 40% by weight, whereby, the polyurethane is free from plasticizers. The fillers make up 50% by weight to 70% by weight of substrate.

[0035] The choice of isocyanate-components of polyurethane depends on the properties of the substrate. The following can be used: for example, toluylene diisocyanate, diphenylmethane- 4,4'- diisocyanate, dicyclohexylmethane-4, 4'- diisocyanate, hexamethylene diisocyanate, isophoron diisocyanate, mixtures of the mentioned isocyanates or chemically derived isocyanates, for example dimerized or trimerized types.

The choice of the components reacting with the isocyanate depends on the properties of the substrate which are to be adjusted depending on the desired requirement profile.

These can be used: for example, all polyester dioles, -trioles and -polyoles, polyether dioles, -trioles and -polyoles, polyether diamines, -triamines, -polyamines, hydroxyl-functionalized polybutadienes and all monovalent alcohols (mono-oles), monovalent amines (mono-amine), polyether-mono-ole, polyether-mono-amine or products that have been derived from the last four mentioned groups.

It has proven to be advantageous if hydroxyl-functionalized polybutadienes, polyester diols, polyester triols, polyester polyols, polyether diols, polyether triols, polyether polyols, polyether diamines, polyether triamines or polyether polyamines have a molecular weight $M_g \geq 1000$ g/mol.

[0036] In addition to the isocyanate-components mentioned above and the components reacting with them, even other educts can be used for the formation of polyurethane without foregoing the underlying thought of the invention.

[0037] In order to accelerate the reaction between the isocyanate-components and the components reacting with isocyanate, all catalysts known to the expert like for e.g., tertiary amines or organic tin compounds can be used.

[0038] Polyurethanes like those described above are mentioned in "Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21: Polyurethanes".

[0039] In an especially preferred embodiment, a NCO/OH- ratio is adjusted to 1.0 to 1.3, preferably 1.0 to 1.1 for the formation of polyurethane.

[0040] The preferred mono-ol-OH-portion with regard to the entire-OH-portion, that means, the preferred chain-terminating component, lies between 5% and 40%, especially between 10% and 30%.

[0041] Reinforced fillers such as carbon black and also non-reinforced fillers, like for e.g. chalk or barium sulfate can be used as fillers. Other examples are talc, mica, pyrogenic silicic acid, silicate, zinc oxide, microballoons, solid glass microbeads, hollow glass microbeads and/or plastic microbeads of all types. Even mixtures of the materials mentioned can be used.

[0042] The microballoons comprise elastic, thermoplastic hollow beads that have a polymer shell. These beads are filled with low-boiling fluids or liquefied gas. Suitable shell polymers are especially acrylonitrile, PVDC, PVC or acrylates. Hydrocarbons such as lower alkanes, for e.g. pentane, are suitable as low-boiling fluid; chemicals like isobutane are used as liquefied gas.

Especially advantageous properties are observed if the microballons have a diameter of $3\mu\text{m}$ to $40\mu\text{m}$ at 25°C , especially $5\mu\text{m}$ to $20\mu\text{m}$.

The capsules expand irreversibly due to the heating effect and expand three-dimensionally. The expansion ends when the internal pressure equals the external pressure. Thus, a closed-cell foam substrate is obtained which excels due to good flow behavior and high restoring forces.

[0043] After thermal expansion due to increased temperature, the microballoons advantageously have a diameter of $20\mu\text{m}$ to $200\mu\text{m}$, especially $40\mu\text{m}$ to $100\mu\text{m}$.

/6

[0044] To enhance the aging stability of polyurethane, this can be mixed with the customary anti-aging agents depending on the application chosen from the class of discoloring and non-discoloring anti-aging agents, and also in the range between 0% by weight and 5% by weight and also can be mixed with known light stabilizers in the range between 0% by weight and 5% by weight or ozone protectants in the range between 0% by weight and 5% by weight.

To achieve freedom from bubbles, drying agents, like for e.g. calcium oxide or molecular sieve- zeolites of formulation can be admixed, especially in the range between 0% by weight and 10% by weight.

[0045] All the mentioned excipients can be used depending on the purpose of usage either alone or in any arbitrary combination for production of polyurethane mass in order to obtain optimum gain of the usage. By using these additives, even black staining is easily possible which is especially required in the automotive industry.

[0046] The A- and B-components can be purchased directly or produced from individual components available commercially according to the customary mixing- or manufacturing process which is in accordance with the prior art, for example, depending on the rheological setting and filler content in a stirring vessel, in a planetary mixer or in a dissolver.

[0047] The special feature of the inventive process is the inverse type of coating. As is customary, an adhesive mass is not applied on a substrate, but a reactive, initially flowing substrate material on an introduced adhesive mass or if necessary, on other incoming materials of which at least one of it is provided with a pressure-sensitive adhesive mass.

[0048] An advantage of this process is that a good anchoring between the polyurethane – substrate and the incoming, web-shaped materials, for e.g. the adhesive mass, is obtained without having to use primers or similar auxiliary layers. This is the case because the polyurethane- substrate is reactive to the isocyanate which was not yet converted immediately at the point of time of coating and therefore, attaches itself chemically spontaneously to many substrates.

[0049] Another advantage is the simplicity of the process which makes it possible to produce even complex structured, i.e. self-adhesive articles containing a composite substrate in a maximum of three coating steps (production of incoming material 1, if

necessary, production of incoming material 2, coating with polyurethane- substrate) with particular cost advantages.

[0050] At the end of the coating with two-component polyurethane, no other coating or laminating step is required for the manufacture of self-adhesive articles.

[0051] Another advantage of the process is to produce a particular diversity of self-adhesive articles. This diversity arises from the diverse possibilities of the polyurethane-chemistry mentioned above and from the diverse possibilities with regard to the incoming materials 1 and 2.

[0052] With the help of the following examples, the invention is described better without wanting thereby to restrict the invention.

[0053] The following test methods were used in order to briefly characterize the specimens manufactured according to the described process:

- The bond strength was determined in accordance with BDF JOPMA002.
According to this method, the adhesive tape sample is applied on the substrate (steel) and finally peeled off under defined conditions in a tensile tester. The peel angle was 180°, the peel speed 300 mm/min. The force required for peeling off is called as the bond strength.
- The determination of tensile strength and elongation at break were determined in the tensile test in accordance with BDF JOPMC001.
In this test, a test strip of 100 mm length and 25 mm width was loaded in a tensile tester with defined clamping speed (300 mm/min) in the longitudinal direction till it tore. The tensile strength with respect to the cross-section of sample and the extension at the point of tear were determined.

- The compression stress value was determined in accordance with DIN 53577, The compression stress value is the compressive stress determined for a defined deformation (14% in the examples) for a stress process. It is determined in a compression test machine. The dimensions of the sample were 30mm x 30mm x 15mm (LxBxH). The height of the sample was adjusted by stacking the adhesive strips.

[0054] The coating was undertaken on an unit of the firm, Pagendarm, in these examples. The unit had the unwinding and winding facilities for the incoming materials 1 and 2 with web width of 50 cm as shown in Figure 1. The coating gap length was variable between 0 and 1 cm. The length of the heated channel was about 12 m. The temperature in the heated channel could be partitioned into four zones and can be freely chosen between room temperature and 120° C.

[0055] A two-component mixing- and dosing unit of the company, Spritztechnik-EMC was used. The mixing system was dynamic. The mixing head was designed for two fluid components and a third gaseous component. The mixing rotor had a variable speed of approximately 5000 rpm maximum. Toothed wheel pumps with a maximum output of about 2 l/min were used as dosing pumps of this unit.

[0056] The A-components were prepared in an evacuable dissolver of the firm, Drais.

Examples

Example 1

[0057] To produce a special masking tape which is used during the coating process in the mass production of window flange- glued joints in the automobile industry after application of the first paint layer (cathodic electrocoating) and to protect it from further coats which are baked at temperatures upto 180°C, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0058] A 23µm thick polyester film (polyethylene terephthalate) was coated in an usual coating process with a known natural rubber-based adhesive mass from a solution with an application thickness of about 25µm and was covered with a commercially available release paper during winding. This adhesive mass consists of:

- 48% natural rubber CV50
- 23% Poly-beta- pinene resin
- 5% Terpene phenolic resin
- 3% rosin resin
- 7% copolymer of acrylonitrile and butadiene
- 8% zinc oxide
- 5% reactive alkyl phenol resin and
- 1% 2,5-Di- (tertiary)- amyl-)hydroquinone.

2nd procedural step, Polyurethane- coating:

[0059] The polyester film provided with the adhesive mass was coated with a degasified, two-component polyurethane- substrate at a speed of 1 m/min in the second procedural step from the non-adhesive side. The application thickness was 120µm. The hardening took place at a channel temperature of 80°C. The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1030® | 30.0 |
| | Arcol 1074 ® | 10.0 |
| | Dibutyl tin dilaurate | 0.2 |
| | Calcium oxide | 5.0 |
| | Bayferrox 3920® | 1.0 |
| | Omyacarb 4BG® | 28.3 |
| B-component | Vestanat IPDI® | 25.5 |

[0060] The adhesive tape so obtained showed a tensile strength of 30.3 N/mm² with an elongation at break of 43.4%. The bond strength on steel was 4.9 N/cm.

The adhesive tape was overpaintable and was sufficiently temperature-stable with regard to paint- baking conditions.

/8

Example 2

[0061] To produce a special masking tape, as used in Example 1 during the coating process in the mass production of window flange- glued joints in the automobile industry after application of the first paint layer (cathodic electrocoating) and to protect it from further coats which are baked at temperatures upto 180°C, and which is further so

flexible that it can be stuck on easily in curves, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0062] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small quantities of known cross-linker, was applied on a commercially available, double-sided release paper in an application thickness of 40 g/m², dried, cross-linked and finally wound up.

2nd procedural step, Polyurethane-coating:

[0063] The acrylate- adhesive mass applied on the release paper was coated directly with a degasified, two-component polyurethane- substrate at a speed of 3 m/min in the second procedural step. The application thickness was 250µm. The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Poly THF 250® | 14.3 |
| | Poly THF 650 ® | 37.6 |
| | Dibutyl tin dilaurate | 0.1 |
| | Calcium oxide | 10.0 |
| | Bayferrox 3920® | 1.3 |
| | Aerosil R 202 ® | 2.0 |
| B-component | Desmodur CD® | 34.7 |

[0064] The adhesive tape so obtained showed a tensile strength of 20.0 N/mm² with an elongation at break of 195%. The bond strength on steel was 2.5 N/cm. The adhesive tape was overpaintable and was sufficiently temperature-stable with regard to paint- baking conditions and could be stuck on even in curves.

Example 3

[0065] For the production of an elastic, sandblast- resistant, punchable stencil- adhesive tape, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0066] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small quantities of known cross-linker, was applied on a commercially available, double-sided release paper in an application thickness of 40 g/m², dried, cross-linked and finally wound up.

2nd procedural step, Polyurethane-coating:

[0067] The acrylate- adhesive mass applied on the release paper was coated directly with a degasified, two-component polyurethane- substrate at a speed of 3 m/min in the second procedural step. The application thickness was 875µm. The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 29.0 |
| | Dibutyl tin dilaurate | 0.1 |
| | Omyacarb 4BG® | 63.1 |
| | Calcium oxide | 5.0 |
| B-component | Desmodur CD® | 2.8 |

[0068] The adhesive tape so obtained showed a tensile strength of 1.7 N/mm² with an elongation at break of 124%. The bond strength on steel was 2.5 N/cm. The adhesive tape was sufficiently resistant to sandblasts and easily punchable.

Example 4

[0069] For the production of a stencil- adhesive tape which had low extensibility at low applied force, was resistant to sandblasts and punchable, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0070] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small quantities of known cross-linker, was applied on a commercially available, slightly creped paper substrate with a basis weight of 68 g/m² in an application thickness of 40 g/m², dried, cross-linked and covered with a commercially available release paper during winding.

2nd procedural step, Polyurethane-coating:

[0071] The slightly creped paper substrate provided with an adhesive mass was coated with a degasified, two-component polyurethane- substrate at a speed of 3 m/min starting from the non-adhesive side in the second procedural step. The application thickness was 850µm. The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 29.0 |
| | Dibutyl tin dilaurate | 0.1 |
| | Omyacarb 4BG® | 63.1 |
| | Calcium oxide | 5.0 |
| B-component | Desmodur CD® | 2.8 |

[0072] The adhesive tape so obtained was sufficiently resistant to sandblasts and was easily punchable. The bond strength on steel was 2.1 N/cm.

Example 5

[0073] For the production of a stencil- adhesive tape which had low extensibility at low applied force, was resistant to sandblasts and punchable, the process was used in the following way:

/10

1st procedural step (preparatory step), Production of incoming material 1:

[0074] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small

quantities of known cross-linker, was applied on a commercially available, 23 μm thick polyester film (polyethylene terephthalate) in an application thickness of 40 g/m^2 , dried, cross-linked and covered with a commercially available release paper during winding.

2nd procedural step, Polyurethane-coating:

[0075] The polyester film provided with an adhesive mass was coated with a degasified, two-component polyurethane- substrate at a speed of 3 m/min starting from the non-adhesive side in the second procedural step. The application thickness was 850 μm . The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 29.0 |
| | Dibutyl tin dilaurate | 0.1 |
| | Omyacarb 4BG® | 63.1 |
| | Calcium oxide | 5.0 |
| B-component | Desmodur CD® | 2.8 |

[0076] The adhesive tape so obtained was sufficiently resistant to sandblasts and was easily punchable. The bond strength on steel was 2.8 N/cm.

Example 6

[0077] For the production of an elastic adhesive tape that can be stuck on easily in curves for general painting- and coating job, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0078] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small quantities of known cross-linker, was applied on a commercially available, double-sided release paper in an application thickness of 40 g/m², dried, cross-linked and finally wound up.

2nd procedural step, Polyurethane-coating:

[0079] The acrylate-adhesive mass coated on the release paper was coated directly with a degasified, two-component polyurethane- substrate at a speed of 3 m/min in the second procedural step. The application thickness was 300µm. The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

/11

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1074 ® | 31.5 |
| | Lutensol A07® | 3.3 |
| | Dibutyl tin dilaurate | 0.1 |
| | Calcium oxide | 7.9 |
| | Omyacarb 4BG® | 53.9 |
| B-component | Desmodur CD® | 3.3 |

[0080] The adhesive tape so obtained showed a tensile strength of 2.1 N/ mm² with an elongation at break of 194%. The bond strength on steel was 2.5 N/cm. The adhesive tape was overpaintable and could be stuck on in curves.

Example 7

[0081] For the manufacture of an edge-protection- adhesive tape, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0082] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small quantities of known cross-linker, was applied on a woven substrate made of thickly woven polyester (20x20 threads per cm in warp- and weft direction, fineness: 34 Nm, basis weight > 130 g/m²) in an application thickness of 40 g/m², dried, cross-linked and covered with a commercially available release paper during winding.

2nd procedural step, Polyurethane-coating:

[0083] The woven fabric provided with the adhesive mass was coated with a degasified, two-component polyurethane- substrate at a speed of 3 m/min starting from the non-adhesive side in the second procedural step. The application thickness was 400µm. The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 29.0 |
| | Dibutyl tin dilaurate | 0.1 |
| | Omyacarb 4BG® | 63.1 |
| | Calcium oxide | 5.0 |
| B-component | Desmodur CD® | 2.8 |

[0084] The adhesive tape so obtained showed a tensile strength of 19.1 N/ mm² with an elongation at break of 24%. The bond strength on steel was 2.9 N/cm.

Example 8

[0085] For the manufacture of an especially cost-effective edge protection- adhesive tape, the process was used in the following way:

/12

1st procedural step (preparatory step), Production of incoming material 1:

[0086] A solvent-based acrylate- adhesive mass, consisting of butyl acrylate (47.5%), ethyl hexylacrylate (47.5%), glycidyl methacrylate (2%), acrylic acid (3%) and small quantities of known cross-linker, was applied on a 150µm thick polyester-spunbonded fabric with a basis weight of 70 g/m² in an application thickness of 40 g/m², dried, cross-linked and covered with a commercially available release paper during winding.

2nd procedural step, Polyurethane-coating:

[0087] The spunbonded fabric provided with the adhesive mass was coated with a degasified, two-component polyurethane- substrate at a speed of 3 m/min starting from the non-adhesive side in the second procedural step. The application thickness was 400 μ m. The hardening took place at a channel temperature of 60 to 70°C.

The composition of the polyurethane – substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 29.0 |
| | Dibutyl tin dilaurate | 0.1 |
| | Omyacarb 4BG® | 63.1 |
| | Calcium oxide | 5.0 |
| B-component | Desmodur CD® | 2.8 |

[0088] The adhesive tape so obtained showed a tensile strength of 9.8 N/ mm² with an elongation at break of 18%. The bond strength on steel was 2.6 N/cm.

Example 9

[0089] For production of a printing plate- adhesive tape for the printing industry, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0090] A solvent-based acrylate- adhesive mass, consisting of ethyl hexylacrylate (70%), stearyl acrylate (17%), acrylic acid (3%) and known resins (10%) was applied on a commercially available, double-sided release paper in an application thickness of 60 g/m², dried and finally wound.

2nd procedural step (preparatory step), Manufacture of incoming material 2:

[0091] Procedural step 1 was repeated.

3rd procedural step, Polyurethane- coating:

[0092] The coating is undertaken between the acrylate- adhesive masses applied on the release paper and obtained from the procedural steps 1 and 2 with a degasified, two-component polyurethane- substrate at a speed of 1 m/min. The application thickness was 1.5 mm. The hardening took place at a channel temperature of 90°C.

The composition of the polyurethane – substrate was as follows:

/13

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 41.0 |
| | Arcol 1043® | 41.0 |
| | Dibutyl tin dilaurate | 0.2 |
| | Kronos 2160® | 1.6 |
| | Calcium oxide | 5.0 |
| | Aerosil R 202® | 3.5 |
| B-component | Vestanat IPDI® | 7.7 |

[0093] The adhesive tape so obtained showed a compression stress value H_{14} of 22 N/cm². The bond strength on steel was 3.4 N/cm.

Example 10

[0094] For manufacture of a microballoon-foamed printing plate- adhesive tape for the printing industry, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0095] A solvent-based acrylate- adhesive mass, consisting of ethyl hexylacrylate (70%), stearyl acrylate (17%), acrylic acid (3%) and known resins (10%) was applied on a commercially available, double-sided release paper in an application thickness of 60 g/m², dried and finally wound.

2nd procedural step (preparatory step), Manufacture of incoming material 2:

[0096] Procedural step 1 was repeated.

3rd procedural step, Polyurethane- coating:

[0097] The coating is undertaken between the acrylate- adhesive masses applied on the release paper and obtained from the procedural steps 1 and 2 with a degasified, two-component polyurethane- substrate at a speed of 1 m/min. The application thickness was 1.5 mm. The hardening took place at a channel temperature of 90°C.

The polyurethane- substrate contained pre-expanded, thermoplastic plastic hollow beads (Expancel ®) and the composition was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1042 ® | 39.5 |
| | Arcol 1043® | 39.5 |
| | Dibutyl tin dilaurate | 0.2 |
| | Kronos 2160® | 1.9 |
| | Calcium oxide | 5.0 |
| | Expancel 551 DE 80® | 3.0 |
| | Aerosil R 202® | 3.5 |
| B-component | Vestanat IPDI® | 7.4 |

[0098] The adhesive tape so obtained showed a compression stress value H_{14} of 30 N/cm². The bond strength on steel was 2.9 N/cm.

Example 11

[0099] For manufacture of nitrogen-foamed, printing plate- adhesive tape for the printing industry, the process was used in the following way:

1st procedural step (preparatory step), Production of incoming material 1:

[0100] A solvent-based acrylate- adhesive mass, consisting of ethyl hexylacrylate (70%), stearyl acrylate (17%), acrylic acid (3%) and known resins (10%) was applied on a commercially available, double-sided release paper in an application thickness of 60 g/m², dried and finally wound.

2nd procedural step (preparatory step), Manufacture of incoming material 2:

[0101] Procedural step 1 was repeated.

3rd procedural step, Polyurethane- coating:

[0102] The coating is undertaken between the acrylate- adhesive masses applied on the release paper and obtained from the procedural steps 1 and 2 with a degasified, two-component polyurethane- substrate at a speed of 1 m/min. Nitrogen was introduced directly at the mixing head in the polyurethane- substrate such that the hardened substrate showed a thickness of 0.7 g/cm³. The application thickness was 1.5 mm. The hardening took place at a channel temperature of 90°C.

The composition of the polyurethane- substrate was as follows:

| | Raw material | Weight fraction [% by weight] |
|-------------|-----------------------|-------------------------------|
| A-component | Arcol 1030 ® | 17.0 |
| | Arcol 1067S® | 40.0 |
| | Dibutyl tin dilaurate | 0.2 |
| | Kronos 2160® | 2.4 |
| | Calcium oxide | 9.0 |
| | Aerosil R 202® | 3.5 |
| B-component | Vestanat IPDI® | 27.9 |

[0103] The adhesive tape so obtained showed a compression stress value H_{14} of 28 N/cm². The bond strength on steel was 2.7 N/cm.

Patent claims

1. Process for continuous production of self-adhesive articles, whereby

- a) a polyol- component is taken in a container A and an isocyanate- component is taken in a container B,
- b) the polyol- and isocyanate-components are mixed in a mixer,
- c) the polyurethane mass thus mixed is applied on a substrate which is coated with a pressure-sensitive adhesive mass; this substrate moves preferably at constant speed,
- d) the laminate, comprising of first substrate, adhesive mass and polyurethane mass is passed through a heated channel in which the polyurethane mass is hardened,
- e) the laminate is wound up in a winding station.

2. Process according to Claim 1, characterized in that a second substrate material is introduced on the polyurethane mass of laminate at preferably constant speed and if necessary, peeled off after the heated channel.
3. Process according to Claim 2, characterized in that the second substrate is provided with a pressure-sensitive adhesive mass.
4. Process according to Claims 1 to 3, characterized in that other containers are made available upstream of the mixer in which catalysts, plasticizers, dyes and other additives may be introduced and added.
5. Process according to the Claims 1 to 4, characterized in that the polyurethane mass is applied on the first substrate which was coated with a pressure-sensitive adhesive mass in such a way that the polyurethane mass is found on the pressure-sensitive adhesive mass.
6. Process according to Claims 1 to 5, characterized in that dehesive media are used as first or second substrates like release paper or release film or paper, fabric, mats, films or elastomer.
7. Single-sided or double-sided, self-adhesive tape, obtained according to a method as per at least one of the earlier claims.

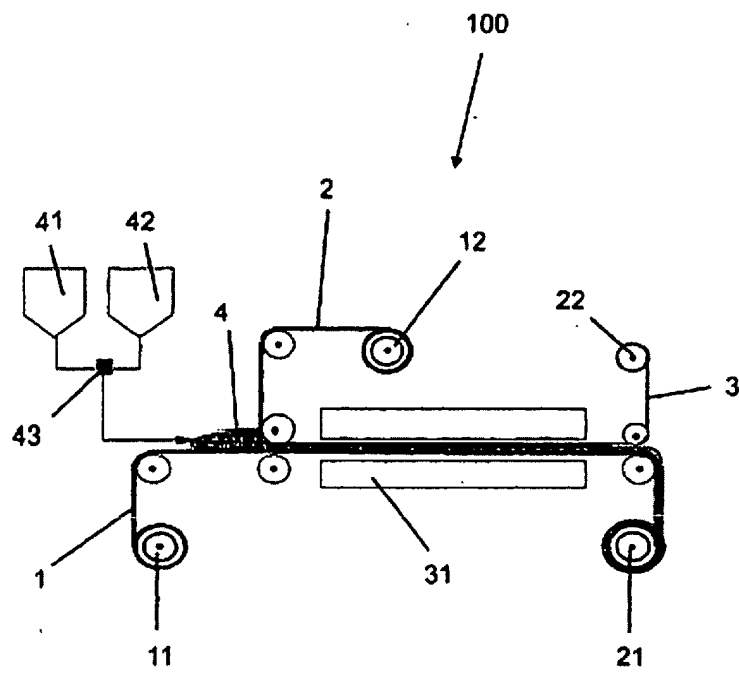


Fig. 1